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**(54) FORMING METHOD FOR ELECTRODEPOSITION COATING FILM, CATIONIC
ELECTRODEPOSITION COATING COMPOSITION, AND ELECTRODEPOSITION COATED ARTICLE**

(57)Abstract:

PROBLEM TO BE SOLVED: To form a coating film which prevents the occurrence of gas pinholes on a steel sheet, especially on a zincified steel sheet or a galvanized steel sheet, and exhibits a high throwing power by specifying the lowest film-forming temperature and electrical conductivity during coating of a cationic electrodeposition coating material.

SOLUTION: Electrodeposition coating is conducted at a set electrodeposition coating temperature and by using a cationic electrodeposition coating material of which the lowest film-forming temperature is adjusted to in the range of $\pm 5^{\circ}\text{C}$ of the set electrodeposition coating temperature (preferably from -2 to 0°C) and of which the electrical conductivity during coating is adjusted to 1,000-1,500 $\mu\text{S/cm}$. The lowest film-forming temperature is adjusted to in the range of $\pm 5^{\circ}\text{C}$ of the set electrodeposition coating temperature e.g. by increasing the mol.wt. of a cationic substrate resin contained in the coating material, The electrical conductivity during coating is adjusted to 1,000-1,500 $\mu\text{S/cm}$ e.g. by partially reacting epoxy terminals with an alkylphenol or a carboxylic acid and cationizing with an amine to decrease the amount of cationization of the cationic substrate resin. The cationic electrodeposition coating material contains the cationic substrate resin, a curing agent, and an organic solvent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the electropainting thing in which the cathodic electrodeposition coat was formed by the cationic electrodeposition paint constituent used for the electrodeposition coat formation method by the cationic electrodeposition paint adjusted to electric conductivity at the time of specific minimum film forming temperature and paint, and this film formation method, and this electrodeposition coat formation method.

[0002]

[Description of the Prior Art]The cationic electrodeposition paint is used for the under coat of an automatic car body or parts.

The pitch powder object which generally contains cationic base resin, a hardening agent, a neutralizer, etc., and the pigment dispersion paste containing pigment dispersion resin and paints are distributed in an aqueous medium, and it is provided.

[0003]When cathodic electrodeposition coating is carried out to a galvanized steel sheet, the abnormalities in-like [crater] may occur in an electrodeposition coat side. In the cationic electrodeposition paint, the hydrogen gas emitted in the electrolysis of water exists between deposit films in early stages of paint, Membrane resistance increases as electrodeposition progresses, if the voltage concerning a coat becomes larger than hydrogen gas discharge voltage, spark discharge will happen, resin of the coat near the discharge hardens with discharge heat, and the phenomenon which becomes insufficient [the heat flow of a coat] and remains as the shape of a crater being unusual is seen. The abnormalities of the shape of this crater are called a gas pin hole, and the character which can control generating of this gas pin hole is called gas pin hole nature.

[0004]Gas pin hole nature poses especially a problem, when coated objects, such as a zinc steel plate with low hydrogen gas discharge voltage, a galvanized steel sheet, and an alloying hot-dip zinc-coated carbon steel sheet, are used. In order to improve gas pin hole nature, the method which make the emitted hydrogen gas easy to add a solvent etc., to form a flexible deposit coat and to escape from is indicated to JP,S60-60169,A and JP,S63-107786,A. However, in these methods, the problem that the circumference nature of per [reverse] fell had arisen. Although the electrodeposited film of a place distant from the polar zone turns into a thin film, without fully being formed, the thing of the performance which thickens thickness of this thin

film part is indicated to be throwing power of electrolytic colouring.

[0005]Then, generating of a gas pin hole is prevented and an electrodeposition paint which does not carry out an adverse effect to performances, such as throwing power of electrolytic colouring, is desired.

[0006]

[Problem(s) to be Solved by the Invention]This invention controls gas pin hole generating to a steel plate especially a zinc steel plate, or a galvanized steel sheet, And it aims at providing the electropainting thing in which the electrodeposition coat was formed by the cationic electrodeposition paint constituent used for the electrodeposition coat formation method with which a high throwing-power-of-electrolytic-colouring coat is obtained, and this method, and this method.

[0007]

[Means for Solving the Problem]This invention persons resulted in this invention, as a result of inquiring wholeheartedly in view of an aforementioned problem. The means for solving a technical problem is the following.

[0008]1. Electrodeposition coat formation method which uses electrodeposition paint which minimum film forming temperature of cationic electrodeposition paint was adjusted to less than **5 ** of electropainting preset temperature, and was adjusted to 1000-1500microS/cm in electric conductivity at time of paint in electropainting, and is electrodeposited with above-mentioned electropainting preset temperature.

2. Electrodeposition coat formation method of above-mentioned description which makes above-mentioned minimum film forming temperature -2-0 ** of above-mentioned electropainting preset temperature.

3. Cationic electrodeposition paint constituent which above-mentioned cationic electrodeposition paint contains cationic base resin, hardening agent, and organic solvent, and is used for electrodeposition coat formation method of above-mentioned description.

4. Electropainting thing in which cathodic electrodeposition coat was formed in substrate of electrodeposition coat formation method of above-mentioned description.

[0009]

[Embodiment of the Invention]Hereafter, this invention is explained in full detail.

[0010]The cationic electrodeposition paint which adjusted minimum film forming temperature to the electropainting preset temperature of less than **5 ** is used for the electrodeposition coat formation method of electrodeposition coat formation method this invention. It becomes easy to escape from the hydrogen gas emitted at the time of electrodeposition coat formation in the above-mentioned minimum film forming temperature being less than **5 ** in electropainting preset temperature, and it is surmised that gas pin hole nature becomes good. If it separates from a mentioned range, a gas pin hole will occur. Compared with the case where minimum film forming temperature's is high when even the above-mentioned minimum film forming temperature of the electropainting preset temperature of less than **5 ** is lower than electropainting preset temperature, a very good result is obtained in respect of workability, especially grinding nonuniformity. It is -2-0 ** of electropainting preset temperature about the above-mentioned minimum film forming temperature preferably.

[0011]On these Descriptions, minimum film forming temperature means the temperature of the electrodeposition paint bath corresponding to the minimal value in thickness in the temperature of an electrodeposition paint bath, and the relation of thickness. Electropainting preset temperature means the temperature set up as a degree of solution temperature of an electro-deposition bath in an electropainting

line.

[0012]In order to adjust to less than 5°C of electropainting preset temperature, the above-mentioned minimum film forming temperature, How to make high the molecular weight of the cationic base resin contained in the above-mentioned electrodeposition paint, How to use aromatic system polyisocyanate or alicyclic polyisocyanate for the polyisocyanate component of the blocked polyisocyanate system hardening agent contained as a hardening agent, In order to make good flow nature at the time of coat formation of the vehicle which furthermore consists of cationic base resin and a hardening agent, there is the method of decreasing the amount of retarder thinner, and it is attained by the adjustment which combined kinds of these methods, or these methods.

[0013]The cationic electrodeposition paint which prepared electric conductivity to 1000-1500microS/cm at the time of paint is used for it while the electrodeposition coat formation method of this invention adjusts the above-mentioned minimum film forming temperature. If voltage is impressed to an electrodeposition paint at the time of electropainting, after big current flows immediately after voltage impressing, it decreases rapidly, and after that, it will gradually decrease and will become stationary current. It is checked that it takes place easily, so that discharge of a hydrogen gas reason has many current amounts which flow immediately after this voltage impressing. Therefore, if the current amount which lowers the electric conductivity of the electrodeposition paint at the time of paint, and flows is stopped, generating of a gas pin hole can be controlled. However, if electric conductivity is too low, it will become difficult to flow through current into a place distant from the polar zone, and throwing power of electrolytic colouring will worsen. Therefore, by adjusting [cm] electric conductivity in 1000-1500 microS /at the time of paint of the above-mentioned electrodeposition paint, gas pin hole nature improves further and high throwing power of electrolytic colouring is obtained. If throwing power of electrolytic colouring worsens and electric conductivity exceeds 1500microS/cm by less than 1000microS/cm at the time of paint, a gas pin hole will occur. Electric conductivity is 1050-1250microS/cm at the time of more desirable paint.

[0014]In order to adjust electric conductivity to 1000-1500microS/cm at the time of paint, After making an epoxy end react in part with alkylphenol or carboxylic acid, There is a method of decreasing the unreacted material (free amine) of the amine made to react when cation-izing the method of cation-izing by amine and making small the amount of cation-izing of cationic base resin or cationic base resin. Electric conductivity can also be adjusted by furthermore carrying out UF filtration of the electrodeposition paint. For example, in order to adjust electric conductivity to a mentioned range, when using the amino modifying epoxy resin produced by aminating an epoxy resin as base resin, the rate of reaction equivalent ratio of a glycidyl group and amine is made into the range of 1.0 / 0.7 - 1.0/0.9. Preparation is still easier, if the half block polyisocyanate which blocked only one functional group of diisocyanate by blocking agents, such as 2-ethylhexyl cellosolve, after the above-mentioned amination is added and free amine is vanished.

[0015]The electrodeposition coat formation method of this invention is the method of electrodepositing the cationic electrodeposition paint which adjusted [above-mentioned] with the above-mentioned electropainting preset temperature by cathodic electrodeposition coating on the surface of the existing conductive substrate. The cathodic electrodeposition coating can apply the method currently performed conventionally and the same method. However, it is necessary to pass one by one in this invention including the process of using the electrodeposition paint adjusted with the above-mentioned adjustment method, and the process electrodeposited with the above-mentioned electropainting preset temperature. It is necessary to specifically

set preferably the minimum film forming temperature of the cationic electrodeposition paint to be used as less than 5°C to electropainting preset temperature at -20°C . As paint conditions, five to 40% of the weight, solids concentration so that it may become 15 to 25 % of the weight preferably, It can dilute with deionized water and the electro-deposition bath which consists pH of the above-mentioned cationic electrodeposition paint of 5.5-8.5 within the limits can be further performed on condition of the impressed electromotive force 100-450V with the electropainting preset temperature of 20°C - 35°C . 5-40 micrometers of within the limits of 10-30 micrometers are suitable for the dry membrane thickness of electropainting preferably. It is suitable to print preferably 100-200 $^{\circ}\text{C}$ of baking temperature of an electrodeposition coat in the range for 10 to 30 minutes at 140-180 $^{\circ}\text{C}$ generally.

[0016]The cationic electrodeposition paint used for the electrodeposition coat formation method of cationic electrodeposition paint constituent this invention contains cationic base resin, a hardening agent, and an organic solvent.

[0017]If the above-mentioned cationic base resin is resin used for a cationic electrodeposition paint, Especially $^{\circ}\text{C}$, for example, an amino group content monomer, copolymerization or the resin which carried out graft polymerization, The resin which added amine to epoxy group content polymer, the resin which onium-salt-ized epoxy group content polymer, Reaction generation resin of dicarboxylic acid and polyamine, the resin which added amine to mallein-ized polymer, the resin which added amine to isocyanate content polymer, the resin which amine-ized the oxazolidone ring content epoxy resin, etc. are mentioned.

[0018]A desirable thing is amino group content resin during illustration of the above-mentioned cationic base resin. the hydroxyl group of the 1st class or the 2nd class and the amino group of the 1st class, the 2nd class, or the 3rd class are specifically included -- amino $^{\circ}\text{C}$ -- 30-100 -- more preferably, It is 40-80 and an average molecular weight is the amino-epoxy resin, amino-poly (meta) acrylate resin, and amino-polyurethane resin of 200-20000. The number of the hydroxyl groups and amino groups which are contained in the above-mentioned cationic base resin may be one, respectively, and two or more kinds may be sufficient as them. When amino $^{\circ}\text{C}$ is less than 30, it is hard to obtain a stable emulsion and 100 is exceeded, electric conductivity becomes high and there is a possibility that gas pin hole nature may fall or a problem may arise in electropainting workability, such as decline in coulomb efficiency and remelting nature.

[0019]It is also preferred during illustration of the above-mentioned cationic base resin to use the modified epoxy resin which contains an oxazolidone ring in intramolecular. This modified epoxy resin can be obtained by carrying out the dealcoholization reaction of the hetero urethane compound to which the screw urethane compound or other active hydrogen compounds to which the diisocyanate compound was made to react were made to react, and the epoxy resin. If the modified epoxy resin containing an oxazolidone ring is used as base resin, the electrodeposition coat and $^{\circ}\text{C}$ resulting from loss on heating will become difficult to happen.

[0020]The above-mentioned hardening agent has a preferred blocked polyisocyanate system hardening agent. In order to adjust minimum film forming temperature to the electropainting preset temperature of less than 5°C , As above-mentioned, aromatic system polyisocyanate or alicycle fellows system polyisocyanate is preferred, and blocks [perfect-] or blocks [partial-] the isocyanate group contained in these polyisocyanate compounds by a blocking agent.

[0021]As the above-mentioned polyisocyanate compound, bis(isocyanatemethyl)cyclohexane, Cyclopentane diisocyanate, cyclohexane diisocyanate, Alicycle fellows system diisocyanate, such as isophorone

diisocyanate and a 2,5(2,6)-bicyclo[2, 2, 1] heptanescrew (isocyanate methyl), Aromatic system diisocyanate, such as tolylene diisocyanate, phenylene diisocyanate, diphenylmethane diisocyanate, and diphenyl ether diisocyanate, is preferred. As these desirable polyisocyanate compounds and a polyisocyanate compound which may be used together, Aromatic aliphatic series system diisocyanate, such as xylylene diisocyanate and diisocyanate diethylbenzene, Trimethyl hexamethylene di-isocyanate, tetramethylene di-isocyanate, Alkylene diisocyanate, such as hexamethylene di-isocyanate.

Tetraisocyanates, such as tri-isocyanate, such as tri-isocyanate toluene, and a diphenyldimethylmethanetetraisocyanate. Polymerization polyisocyanates, such as a dimer of tolylene diisocyanate, or a trimer. To the various above-mentioned polyisocyanate compounds, ethylene glycol, propylene glycol, The end isocyanate content compound etc. which are produced by making low molecule active hydrogen content organic compounds, such as a diethylene glycol, trimethylolpropane, hydrogenation bisphenol A, hexanetriol, glycerin, pentaerythritol, castor oil, and triethanolamine, react are mentioned.

[0022]As a blocking agent used for the above-mentioned blocking, Phenols, lactam, oxime, alcohols, amino alcohol, Active methylene content compounds, such as amines or imide, diethyl malonate, methyl acetoacetate, and ethyl acetoacetate, mercaptans, acid amides, imidazole derivatives, urea, carbamate, and sulfite salt are mentioned.

[0023]When using a dissociation catalyst for dissociation of the blocking agent of the above-mentioned blocked polyisocyanate hardening agent, Metal salt, such as organic tin compounds, such as dibutyltin laurate, dibutyltin oxide, and dioctyl tin, amines, such as N-methylmorpholine, lead and strontium of acetic acid, cobalt, and copper, can be used. The concentration of a dissociation catalyst is 0.1 to 6 weight section to the coat formation resin (sum total of base resin and hardening agent) 100 solid-content weight section in a cationic electrodeposition paint.

[0024]Base resin / hardening agent solid content ratio twists preferably 50/of the above-mentioned cationic electrodeposition paints 50 - 90/10, and they are 60 / 40 - 80/20 preferably. When it separates from the above-mentioned rate, hardenability has a possibility of producing a problem.

[0025]Neutralization and aqueous-ization of the above-mentioned cationic electrodeposition paint cationic base resin and a hardening agent, It is carried out by distributing inorganic acid, such as water soluble organic acids, such as formic acid, acetic acid, propionic acid, lactic acid, citrate, malic acid, tartaric acid, and acrylic acid, or chloride, phosphoric acid, and sulfamic acid, in the aqueous medium included as a neutralizer.

[0026]The above-mentioned cationic electrodeposition paint as an organic solvent which adjusts minimum film forming temperature although water is used as a solvent, Ethylcellosolve, propyl cellosolve, butyl cellosolve, 2-ethylhexyl cellosolve, n-hexyl cellosolve, methanol, ethanol, isopropyl alcohol, n-butanol, isobutanol, ethyleneglycol dimethyl ether, Diacetone alcohol, acetone, methyl ethyl ketone, methoxybutanol, Organic solvents of water immiscibility, such as the organic solvent of water miscibility, such as dioxane and ethylene glycol monoethyl ether acetate, xylene, toluene, methyl isobutyl ketone, hexane, a carbon tetrachloride, 2-ethylhexanol, isophorone, cyclohexane, and benzene, are used. Preferably, it can be considered as desired minimum film forming temperature by making the content ratio low using retarder thinner. Desirable organic solvents for that are ethylcellosolve, propyl cellosolve, butyl cellosolve, 2-ethylhexyl cellosolve, and n-hexyl cellosolve, and the quantity of an organic solvent, Per coat formation resin (sum total of base resin and hardening agent) 100 solid-content weight section and 0.1 to 10 weight section

are preferred.

[0027]The above-mentioned cationic electrodeposition paint may contain a cross-linking resin particle, paints, and various additive agents other than the above-mentioned ingredient if needed. By adding the above-mentioned cross-linking resin particle, the thickness maintenance effect of the edge part of the substrate painted can be promoted. As the above-mentioned cross-linking resin particle, although you may be which resin, such as an acrylic resin, an epoxy resin, phenol resin, and melamine resin, it is preferred that they are especially the cross-linking particles using the ease of a process to an acrylic resin. The 0.02-30-micrometer particle of mean particle diameter is preferred. As the above-mentioned paints, color pigments, such as titanium oxide, red ocher, and carbon black, Extenders, such as aluminum silicate and precipitated barium sulphate, and molybdophosphoric acid, and aluminum, The second iron, titanium, a zirconium, manganese, cobalt, nickel, Molybdophosphate which is a salt with bivalence, such as copper, zinc, and silicon, or a trivalent metal salt, The condensed-phosphoric-acid salt and concrete target which are Tripoli phosphoric acid, metaphosphoric acid, pyrophoric acid, etc. the above-mentioned bivalence, or a salt with a trivalent metal salt can also add rust preventive pigments, such as Tripoli phosphoric acid 2 hydrogen aluminum, metaphosphoric acid aluminum, and the 2nd iron of Pirro phosphoric acid. It faces adding paints and resin for pigment dispersion may be used.

[0028]The coated article of electropainting thing this invention is obtained with the above-mentioned electrodeposition coat formation method. By passing through the above-mentioned process one by one, the coat which gas pin hole generating is controlled and has high throwing power of electrolytic colouring is obtained, and it becomes a high corrosion resistance electropainting thing by high appearance. According to the purpose and a use, the obtained electropainting thing can form a second coat coat, a glazing coat, or a glazing coat one by one, and can be used.

[0029]

[Example]Next, although working example and a comparative example are given and this invention is explained still more concretely, this invention is not limited only to these working example.

[0030]In 5 mouth flask provided with example of manufacture 1 reflux condenser, the agitator, the dropping funnel, and the nitrogen introducing pipe. 222 copies of isophorone diisocyanate, 99 copies of methyl isobutyl ketone (it omits the following "MIBK".), and 0.2 copy of dibutyltin dilaurate were taught, temperature up was carried out to 50 **, it maintained and 174 copies of methylethyl ketoxime was dropped at this so that an internal temperature might not exceed 70 **. After the end of dropping, after holding at 70 ** for 1 hour until the peak of the isocyanate group disappeared by the IR spectrum, it cooled and the blocked polyisocyanate hardening agent was prepared. Solid content was 80%.

[0031]the example 2 of manufacture -- the same reaction vessel as the example 1 of manufacture prepared independently -- liquid epoxy resin (the Dow Chemical Co. make.) of the weight per epoxy equivalent 188 Trade name "DER-331J"681 weight section, 269 copies of bisphenol A, 88 copies of nonyl phenol, and 115 copies of MIBK(s) were taught, and it warmed at 140 **, and was made to dissolve thoroughly. After adding five copies of 2-ethyl-4-methylimidazole 2% solutions (xylene 98%) as a reaction catalyst, making it react at 140-150 ** and adding 146 copies of MIBK(s) by making the weight per epoxy equivalent 1210 into a terminal point, it was made to cool to 105 **. Subsequently, 54 copies of methyliso butylene ketimines (73% MIBK solution) of 47 copies of n-methylethanol amine and diethylenetriamine were added, it was kept warm at 120 ** for 1 hour, and cationic base resin was obtained.

[0032]340 copies of hardening agents and 55 copies of n-hexyl cellosolves which were obtained in the example 1 of manufacture to 1405 copies of cationic base resin obtained in the example 2 of example of manufacture 3 manufacture are mixed at 90 ** for 30 minutes, After 14.6 copies of formic acid neutralized 88%, it diluted with 1985.4 copies of deionized water slowly, the organic solvent was removed under decompression, and solid content 36.0% of epoxy emulsion X was obtained.

[0033]The example 4 (for comparative examples) of manufacture

340 copies of hardening agents and 140 copies of n-hexyl cellosolves which were obtained in the example 1 of manufacture to 1405 copies of cationic base resin obtained in the example 2 of manufacture are mixed at 70 ** for 30 minutes, After 16.7 copies of formic acid neutralized 88%, it diluted with 1898 copies of deionized water slowly, the organic solvent was removed under decompression, and the epoxy emulsion Y of 36.0% of solid content was obtained.

[0034]The example 5 (for comparative examples) of manufacture

340 copies of hardening agents and 55 copies of n-hexyl cellosolves which were obtained in the example 1 of manufacture to 1405 copies of cationic base resin obtained in the example 2 of manufacture are mixed at 70 ** for 30 minutes, After 20.9 copies of formic acid neutralized 88%, it diluted with 1979 copies of deionized water slowly, the organic solvent was removed under decompression, and the epoxy emulsion Z of 36.0% of solid content was obtained.

[0035]

Example of manufacture 6 ** Amount 2-ethylhexanol half block-ized of part weight section solid content

320.0 304 toluene diisocyanate (inside of MIBK)

Dimethylethanolamine 87.2 87.2 lactic acid solutions 117.6 88.2 ethylene-glycol-monobutyl-ether 39.2

According to the - above-mentioned presentation, 2-ethylhexanol half block-ized toluene diisocyanate (inside of MIBK) was added to dimethylethanolamine at the room temperature using the suitable reaction vessel.

The mixture generated heat and agitated this for 1 hour. Subsequently, lactic acid was prepared, the reaction mixture was further agitated for butyl cellosolve at 65 ** for an hour half [about], and the fourth class-ized agent was obtained.

[0036]

** Amount bisphenol A type epoxy resin of part weight section solid content 710.0 681.2 (the weight per epoxy equivalents 193-203, the ShellChemical company company make, trade name "Epon 829")

Bisphenol A 289.6 289.62-ethylhexanol half block-ized 406.4 386.1 toluene diisocyanate (inside of MIBK)

Fourth class-ized agent 496.3 421.9 deionized-water 71.2 ethylene-glycol-monobutyl-ether 1584.1 According to the - above-mentioned presentation, a bisphenol A type epoxy resin and bisphenol A were taught to the suitable reaction vessel, and were heated to 150-160 ** under a nitrogen atmosphere. The initial exoergic reaction occurred. The reaction mixture was made to react at 150-160 ** for about 1 hour, it ranked second, and 2-ethylhexanol half block-ized toluene diisocyanate was added to 120 ** after cooling. The reaction mixture was kept at 110-120 ** for about 1 hour, it ranked second and butyl cellosolve was added.

Subsequently, it cooled and equalized at 85-95 **, and the fourth class-ized agent manufactured further previously was added. The mixture was held at 85-95 ** until acid value was set to 1, and the varnish for pigment dispersion was obtained. Resin solid content was 50%.

[0037]50 copies of varnishes for pigment dispersion, 93 copies of deionized water which were obtained in the example 6 of example of manufacture 7 manufacture, 1.8 copies of carbon black, seven copies of dibutyl tin

oxide, 20 copies of kaolin, six copies of lead silicates, and 72.2 copies of titanium dioxides were mixed, and the SANDOGU lined mill distributed, it ground until it became a particle size of 10 micrometers or less, and the pigment dispersion paste was obtained.

[0038]The emulsion X, Y, or Z, the pigment dispersion paste, and deionized water which were obtained in working example 1-3 and the example of manufacture mentioned above comparative example 1-2 were blended according to the presentation shown in Table 1, and the diluted paint of working example 1-3 and the comparative examples 1-2 was obtained. The paint of working example 2 sampled the filtrate for the paint of working example 1 15% by UF filtration, and the paint which adjusted electric conductivity to 1100microS/cm was used for it by supplying the sampled quantity with pure water. The evaluation result about the minimum film forming temperature of each diluted paint, paint electric conductivity, solid content, electropainting preset temperature and the gas pin hole nature of each diluted paint, throwing power of electrolytic colouring, and workability is shown in Table 1. The valuation method by gas pin hole nature, throwing power of electrolytic colouring, and workability is as below-mentioned.

[0039](Gas pin hole nature) To the alloying hot-dip zinc-coated carbon steel sheet which performed chemical conversion. After electrodepositing the pressure-up back in 5 seconds and electrodepositing the paint of each working example or a comparative example in 175 seconds, respectively to 200V, 220V, 240V, 260V, 280V, and 300V, it rinsed, and burned for 10 minutes at 160 **, and the painted-surface state was observed. Gas pin hole nature can estimate that it is good, so that the voltage which the crater generated is high.

[0040](Throwing power of electrolytic colouring) What is called a four-sheet box method estimated throwing power of electrolytic colouring. Namely, as shown in drawing 1, the zinc phosphate treated steel sheets (surfboard dyne SD-5000 (made by Nippon Paint Co., Ltd.) processing of JIS G 3141 SPCC-SD) 11-14 of four sheets, It arranges in parallel at intervals of 20 mm in the state where it stood, and the box 10 which sealed the both-side-surfaces lower part and the bottom with insulators, such as cloth adhesive tape, is used. The through hole 15 of 8 mmphi is formed in steel plates 11-13 other than steel plate 14 at the lower part. This box 10 is immersed in the electropainting container 20 to which the electrodeposition paint 21 of each working example or a comparative example was paid, as shown in drawing 2, and it is made for the diluted paint 21 to invade in the box 10 only from each through hole 15. And each steel plate was electrically connected, and the counter electrode 22 has been arranged so that distance with the nearest steel plate 11 may be set to 150 mm. Each steel plates 11-14 were used as the negative pole, voltage was impressed by having used the counter electrode 22 as the anode, and cathodic electrodeposition coating was performed to the steel plate. The thickness of the coat formed in A side of the steel plate 11 in 5 seconds after an impression start carried out pressure up of the paint to the voltage which amounts to 20 micrometers, and it was performed by maintaining the voltage for 175 seconds after that. The electropainting preset temperature at this time was adjusted at 28 **. The thickness of the coat which burned it for 20 minutes at 160 ** after rinsing each steel plate after paint, and was formed in A side of the steel plate 11 nearest to the counter electrode 22 after air cooling, The thickness of the coat formed in G side of the furthest steel plate 14 from the counter electrode 22 was measured, and the ratio (G/A value) of thickness (G side)/thickness (A side) estimated throwing power of electrolytic colouring. Throwing power of electrolytic colouring can estimate that it is good, so that this value is large.

[0041](Workability) In the center section of the same zinc phosphate treated steel sheet as what was used for evaluation of the above-mentioned throwing power of electrolytic colouring, about 2 cm in width. The

range 10 cm in length so that it may **** with the abrasive paper of #400 and grinding slag may not remain. After rinsing, After making it fully dry, with the paint preset temperature in each working example and a comparative example, perform electropainting for [impressed-electromotive-force 200 - 250] V or 3 minutes so that dry membrane thickness may be set to 20 micrometers, and each steel plate after paint, After rinsing, it burned for 20 minutes at 160 **, the visual judgment of the paint film appearance was carried out after air cooling, and it judged by the following judging standards.

O -- Grinding-nonuniformity-less ** -- x to which grinding nonuniformity is accepted somewhat -- Grinding nonuniformity is accepted notably. [0042]

[Table 1]

		実施例			比較例	
		1	2	3	1	2
塗料	エポキシエマルション(g)	X	384	384	384	—
		Y	—	—	—	384
		Z	—	—	—	442
	顔料分散ペースト(g)		117	117	117	135
	脱イオン水(g)		499	499	499	423
	合計(g)		1000	1000	1000	1000
	最低塗膜温度(°C)		27	29	27	27
	塗装時電導度(μS/cm)		1230	1100	1230	1390
	固形分(%)		20.0	19.8	20.0	23.0
	塗装設定温度(°C)		30	30	25	30
評価	ガスピンホール性(V)		300以上	300以上	300以上	220
	つきまわり性		0.56	0.62	0.60	0.30
	作業性(研ぎムラ)		O	O	Δ	O

[0043] So that clearly from the result of Table 1 this examples 1-3, By having adjusted the minimum film forming temperature of the cationic electrodeposition paint to the electropainting preset temperature of less than **5 **, and having adjusted electric conductivity to 1000-1500microS/cm at the time of paint, it becomes easy to escape from the hydrogen gas emitted at the time of electrodeposition coat formation, and the coat which gas pin hole nature becomes good, and has high throwing power of electrolytic colouring was obtained. Since minimum film forming temperature is lower than electropainting preset temperature, working example 1 and 2 is a point of workability, especially grinding nonuniformity, and the very good result was also obtained. On the other hand, according to the comparative example 1, since the minimum film forming temperature of the cationic electrodeposition paint had separated from less than **5 ** of electropainting preset temperature, since 1000-1500microS/cm had separated from electric conductivity at the time of paint, by the comparative example 2, gas pin hole nature and throwing power of electrolytic colouring brought a result which is not good.

[0044]

[Effect of the Invention] In this invention, the minimum film forming temperature of a cationic electrodeposition paint is adjusted to less than **5 ** of electropainting preset temperature, and electric conductivity is adjusted to 1000-1500microS/cm at the time of paint.

Therefore, it becomes easy to escape from the hydrogen gas emitted at the time of electrodeposition coat formation, gas pin hole nature becomes good, and the film formation method of the cationic electrodeposition paint with which the coat which gas pin hole generating is controlled and has high throwing power of electrolytic colouring is obtained can be provided.

[Translation done.]

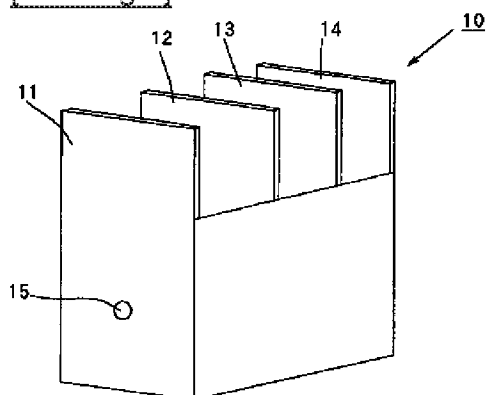
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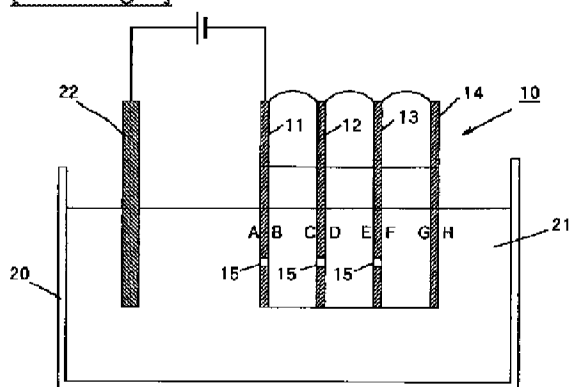
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]